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The *Teff* straw: a novel low-cost adsorbent for quantitative removal of Cr(VI) from contaminated aqueous samples

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ABSTRACT

In the present study, removal of Cr(VI) from aqueous solutions was investigated utilizing *Teff* straw, the agricultural solid waste product of Tef [Eragrostis tef (Zucc.) Trotter]. The characteristic surface chemistry of the *Teff* straw was analyzed by FT-IR analysis and the adsorption efficiency of this novel adsorbent was studied using the batch adsorption technique. Different experimental parameters including pH, contact time, adsorbent dose, initial metal ion concentration, and agitation speed were optimized. Equilibrium and kinetic models for Cr(VI) sorption were studied by considering the effects of concentration and contact time at the optimum pH (pH = 2) and agitation speed of 150 rpm. Results of the sorption equilibria were found to fit better to the Langmuir isotherm ($R^2 = 0.9739$) than the Freundlich isotherm ($R^2 = 0.9187$) and maximum Cr(VI) loading capacity of 3.51 mg/g was determined. On the other hand, kinetics of Cr(VI) sorption on the *Teff* straw was well defined by the pseudo-second order model ($R^2 = 0.9999$). The results obtained showed that the use of *Teff* straw can be considered as one of the most promising, natural, easily accessible, and low-cost adsorbent for efficient and quantitative removal of Cr(VI) from contaminated wastewaters released from leather industries.

Keywords: Adsorption isotherm; Adsorption kinetics; Cr(VI); FT-IR; *Teff* straw

1. Introduction

Toxic metals originated from a variety of sources including industrial discharges, domestic sewage, non-point runoff, urban storm runoff, and atmospheric precipitation are moving through the environmental compartments and primarily joining the surface water bodies. The major feature that distinguishes toxic metals from other pollutants includes their inherent behavior described by their persistence in the environment [1]. As a consequence, they are known to cause serious water pollution and becoming common threat to the environment and the inhabitants of the ecosystem. To minimize and, whenever possible, to prevent the risks due to toxic metals, it is very important to systematically identify the sources and take the necessary measures in order to minimize or stop uncontrolled discharges. As this may not be easily achieved, giving prior attention should be the major concern for developing technical know-how for their removal from metal bearing effluents before they contaminate the water bodies and natural streams [2].

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In the recent years, discharge of toxic metals into the environment has been reduced in several countries due to the more stringent legislations, improved cleaning technologies, and altered industrial activities. However, the demand for developing economical and environmentally friendly methods for removal of toxic metals is still requiring considerable attentions [2]. One of the most commonly known toxic metals discharged into the environmental water bodies, from several industries, is chromium. Chromium has both useful and detrimental properties. In the environment, chromium occurs mainly in the oxidation states of + III and + VI, which have contrasting toxicities, mobilities and bioavailabilities [3]. Cr(III) is an essential trace element needed for glucose metabolism in humans, animals, and plants and it is relatively innocuous and immobile. However, Cr(VI) moves rapidly through the soils and aquatic environments and is also a strong oxidizing agent that is capable of being absorbed through the skin [4,5].

Quite a number of analytical methods have been employed for the removal of toxic metal ions from aqueous wastes including chemical precipitation [6], ion exchange [7–9], membrane technology [10], adsorption on activated carbon [11], etc. Each of these methods has its own merits and demerits. Chemical precipitation is ineffective, especially when the metal ion concentration in the aqueous solution is lower than 50 mg/l. Moreover, such treatments produce large amounts of sludge to be treated with great difficulties [12]. Ion exchange, membrane technologies, and activated carbon adsorption processes are rather expensive. Therefore, research directions should be geared toward the search for newer and cost-effective technologies for removal of toxic metals from wastewaters and in this regard, the use of biosorbents seems a promising alternative as the drawbacks noted with the earlier techniques mentioned could significantly be minimized [12].

Biosorption is a process that utilizes inexpensive dead biomass to sequester toxic heavy metals and is particularly useful for removal of contaminants from industrial effluents. The capacity of certain types of microbial and seaweed biomass to remove and concentrate toxic heavy metals from various solutions provide the basis for cost-effective technology in the treatment of industrial effluents [13]. The search for a low-cost and locally available adsorbent has led to the selection of materials from agricultural and biological origin, along with industrial by-products as adsorbents to greatly reduce the levels of toxic heavy metals to environmentally acceptable limits in economical manner. Agricultural residues such as wheat bran [14], walnut, hazelnut, and almond shell [15], rice husk [16], rice straw [17], barley hull [18], sugarcane bagasse [19], sawdust of wood and wheat straw [20], and Almond Green Hull [21] have been applied as efficient adsorbents for Cr(VI) removal from contaminated aqueous samples.

In the present study, *Teff* straw, an agricultural solid waste obtainable from Tef [Eragrostis tef (Zucc.) Trotter] was utilized for the removal of Cr(VI) from aqueous samples. *Teff* is an indigenous cereal crop mainly produced in Ethiopia with the largest share of farmlands used for cereal cultivation (22.7% or 2.4 million hectares) and the third (i.e. after maize and wheat) in terms of annual grain production (16.3% or 24.4 million quintals) [22]. It is a fine stemmed, tufted annual grass characterized by a large crown, many shoots, and a shallow diverse root system. It is the smallest grain in the world; 150 grains to weigh as much as one grain of wheat. The extremely small grains are 1–1.5 mm long and there are 2,500–3,000 seeds in one gram of it [23].

The principal use of *Teff* grain as food item is primarily known in Ethiopia, as a specially prepared Ethiopian bread called *Injera*. *Injera* is one of the most common staple foods, and known to provide approximately two third of the diet for the population. Baking *Injera* undergoes the following processes: the grain is ground into flour, fermented and made into sour–dough type which is baked onto a clay plate to give a soft flat bread. Moreover, *Teff* straw from threshed grains is considered to be animals' forage and superior to straws from other cereal species in Ethiopia. It is also utilized to reinforce the mud used for covering the wooden materials, during construction of houses, mainly in the countryside. From a number of plant materials reported for adsorption of toxic heavy metals so far, no studies have been performed on the *Teff* straw. In the present study, attempts have been made to investigate the possibility of using *Teff* straw as sustainable adsorbent for Cr(VI) uptake from synthetic wastewater samples.

To this end, series of systematic experimental procedures have been developed for quantitative removal of Cr(VI) from synthetic wastewater samples utilizing the *Teff* straw as an adsorbent. Furthermore, the effects of various experimental parameters influencing the removal efficiency of Cr(VI) using the proposed adsorbent have been investigated. Appropriate equilibrium and kinetic models for Cr(VI) sorption onto the *Teff* straw were also studied and determined experimentally.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals used in this study were of analytical–reagent grade and were used as received, i.e. without any further purification. Potassium dichromate, $K_2Cr_2O_7$, (Assay ≥ 99.8%), was purchased from Riedel-de Haen, Germany. The stock standard solution (1,000 mg/l) of Cr(VI) was prepared by dissolving 0.566 g of $K_2Cr_2O_7$ in 200 ml volumetric flask and made up to the mark using distilled–deionized water. All the required working solutions of Cr(VI) were prepared from the intermediate stock solution by appropriate dilution. The sample solution pH was adjusted by adding drops of either NaOH or HNO_3 (0.1 mol/l each) solution whenever required [24].

2.2. Instrumentation

The atomic absorption spectrometer used in the current study was AAnalyst 600 model (Perkin–Elmer, USA) equipped with both deuterium-arc background corrector and Zeeman correction devices, a transversely-heated graphite furnace atomizer, AS-800 autosampler, and hallow cathode lamp. Argon (99.999% purity) was used as inert gas, with a flow rate of 250 ml/min during the whole analyses periods, except during atomization where the flow was stopped. Adwa pH meter (AD1020 pH/mv/ISE/Temperature, Hungary) was used for the sample pH adjustment. Identification of the various functional groups of the *Teff* straw sample was accomplished using Spectrum 65 FT-IR spectrometer (Perkin Elmer, USA). The instrumental parameters used as well as the furnace heating programs of the graphite furnace atomic absorption spectrometer (GFAAS) are shown in Table 1.

2.3. Collection and preparation of the Teff straw samples

The *Teff* straw samples were collected locally from Addis Ababa using pre–cleaned polyethylene bags. The *Teff* crop, while it is on the farm and the straw obtained after the crop has been harvested, is shown in Fig. 1. The straw samples were air dried and cut into smaller pieces to reduce the size and then washed five times with distilled water to remove dust particles and other soluble impurities [25]. After drying, the samples were ground with an electric mill and allowed to pass through 150 μm sieve. The powdered samples were dried at 105 ℃ for 24 h in an oven until constant mass of the powdered sample was obtained.

2.4. Equilibrium adsorption studies

Batch mode adsorption studies were carried out by agitating 50 ml of the synthetic waste solutions containing different concentrations of Cr(VI) in 100 ml Erlenmeyer flasks, having adsorbent masses of 0.1–0.7 g on automatic shaker at room temperature. The content was left to stand for 1 h until equilibrium was established, and then the supernatant was carefully filtered through Whatman No. 42 filter paper which was pre–saturated with distilled water [26]. Then, the effects of the major experimental parameters on the adsorption of Cr(VI) on the *Teff* straw were investigated. The equilibrium metal concentrations were determined in terms of absorbance measurement using GFAAS. Finally, the signals obtained as such were computed in terms of the metal ion concentration using standard calibration curve. In all cases, the adsorption capacity at equilibrium, q_e (mg/g), of Cr (VI) was calculated using the following relation:

$$q_e = (C_o - C_e)\frac{V}{W} \tag{1}$$

where C_o and C_e (mg/l) are the liquid-phase concentrations of Cr(VI) at initial period and equilibrium, respectively. V is the volume (l) of the sample solution and W is the weight (g) of the dry sorbent. Similarly, the percentage of adsorption of Cr(VI) on the *Teff* straw was determined utilizing the following equation [27]:

$$\%\ Adsorption = \frac{(C_o - C_e)}{C_o} \times 100 \tag{2}$$

Table 1
Graphite furnace temperature program for determination of Cr(VI) (wavelength 357.9 nm, slit width 0.7 nm, lamp current 30 mA and sample volume 20 μl)

Step	Temperature (℃)	Ramp time (S)	Hold time (S)	Argon flow rate (ml/min)
Drying	110	1	30	250
Pyrolysis	500	10	20	250
Atomization	2,000	0	5	0
Cleaning	2,450	1	3	250

Fig. 1. *Teff* crop on the farm (left) and *Teff* straw after harvest (right).

3. Results and discussion

3.1. FT-IR analysis of Teff straw

To understand the mechanism of metal binding process on the natural adsorbents, the different functional groups found in the sorbent material are the key factors [28]. Hence, to identify the types of functional groups in the *Teff* straw responsible for the Cr(VI) uptake, an FT-IR analysis, on the solid phase, was carried out on the powdered adsorbent prepared in a KBr disk. The FT-IR spectra Fig. 2 of the *Teff* straw before (A) and after (B) the metal uptake show a number of different absorption peaks, indicating the complex nature of the *Teff* straw. The spectra of the adsorbent were measured within the range of 4,400–400 cm^{-1} and the absorption peak around 3,467 cm^{-1} indicates the existence of O–H groups. The peaks at 2,920 cm^{-1} can be assigned to the stretching vibration of the C–H groups. The absorption peaks at 1,747, 1,627, 1,376, and 1,084 cm^{-1} may be associated with the presence of C=O, C=C, and C–O functionalities, respectively [29]. As shown in Table 2, the major absorption peaks in the sample after adsorption have undergone a change in their absorption bands intensity and frequency confirming participation of these functional groups in the adsorption of Cr(VI) by the *Teff* straw.

3.2. Effect of different experimental parameters on adsorption of Cr(VI) on the Teff straw

3.2.1. Effect of pH on adsorption of Cr(VI)

Aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the sorbent. Hence, metal sorption is critically linked to the pH of the sample solution [26] and influences the solution chemistry of heavy metals (i.e. hydrolysis, complexation, redox reactions, and precipitation) [30]. During Cr(VI) adsorption, pH of the system controls the adsorption capacity due to its influence on the surface properties of the adsorbent and ionic forms of chromium in the solutions [19]. In the current study, the effect of pH was studied in the pH range of 2–9 [25]. The experiments were carried out with 50 ml of 5 mg/l solutions of Cr(VI) using 0.6 g powdered *Teff* straw in 100 ml Erlenmeyer flask. Cr(VI) adsorption by *Teff* straw as a function of solution pH is given in Fig. 3 and the results indicated higher removal efficiency at lower pH values. However, there was a sharp decrease in the percentage of adsorption beyond pH 2, reaching the minimum at pH 9. The highest percentage removal of Cr(VI) was obtained at pH 2 which was found to be 92.51%. Therefore, pH 2 was utilized as the optimal pH for the subsequent experiments. Similar result was also reported in other study [4].

In the pH range 1–6, chromium ions exist in different forms, such as $Cr_2O_7^{-2}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, and $Cr_4O_{13}^{2-}$ of which $HCrO_4^-$ predominates. As pH of the solution increased, the predominant species were CrO_4^{2-} and $Cr_2O_7^{2-}$ [31]. More adsorption at acidic pH indicates that the lower pH results in an increase in H^+ ions on the adsorbent surface that results in significantly strong electrostatic attraction between positively charged adsorbent surface and the chromate ions [32]. On the other hand, lesser adsorption of Cr (VI), at pH greater than 6, may be due to the dual competition of both the anions, CrO_4^{2-} and OH^-, to be adsorbed on the surface of the adsorbent, of which OH^- predominates [19].

Fig. 2. FT-IR spectra of the *Teff* straw in KBr disc; before Cr(VI) loading (A) and after Cr(VI) loading (B).

Table 2
The FT-IR spectral characteristics of the *Teff* straw before and after adsorption

IR Peak	Absorption bands (cm^{-1}) Before adsorption	After adsorption	Differences	Functional group Assignment
1	3,467	3,359	−108	Bonded O–H group
2	2,920	2,929	+9	Aliphatic C–H group
3	1,747	1,736	−10	C=O Stretching
4	1,627	1,630	+3	Unsaturated C=C groups
5	1,376	1,383	+7	Carboxyl group
6	1,084	1,088	+4	C–O Stretching

3.2.2. *Effect of agitation speed on the removal efficiency of the* Teff *straw*

The removal efficiency of the adsorbent for a given metal ion generally increases with increasing agitation speed [5]. The increase in speed of agitation decreases the time required for the adsorbate to equilibrate, by decreasing the boundary layer resistance to mass transfer and hence increases the diffusion rate of the adsorbate from the bulk into the adsorbent particles [33]. In the current study, agitation speed was varied from 50 to 200 rpm while keeping the solutions at pH 2. The percentage uptake of Cr(VI) by the *Teff* straw increased from 66.34 to 80.32% when agitation speed increased from 50 to 150 rpm and then remained almost constant for agitation speed up to 175 rpm followed by a decrease beyond 175 rpm. As shown in

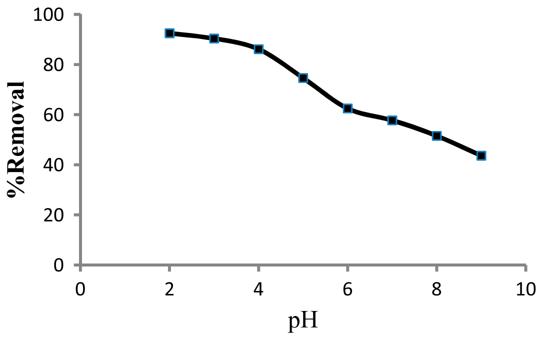

Fig. 3. Effect of pH on percentage removal of Cr(VI) using *Teff* straw.

Fig. 4, increase in the agitation speed improved the diffusion of the Cr(VI) ions toward the surface of the adsorbents as revealed by the increase in the percentage removal and reached a maximum at 150 rpm. However, with vigorous increase in agitation speed, the adsorbed metal ions tend to undergo desorption [34]. Hence, agitation speed of 150 rpm was selected as the optimum value.

3.2.3. Effect of contact time on adsorption of Cr(VI) on the Teff straw

The effect of contact time on the adsorption of Cr(VI) from aqueous solutions to the *Teff* straw was investigated and the experimental results are shown in Fig. 5. There was a fast increase in the percentage removal upon increasing the contact time from 10 to 60 min. This could possibly be due to the time needed for the adsorption equilibrium to be established [5]. However, beyond 60 min, the percentage removal remained nearly constant and the percentage removal of Cr(VI) by the *Teff* straw at 60 min was found to be 97.8%. Therefore, a contact time of 60 min was selected as optimum.

3.2.4. Effect of adsorbent dose

The removal efficiencies of the *Teff* straw for Cr(VI), in 50 ml of 5 mg/l sample solutions, were investigated at different adsorbent doses, i.e. 0.1–0.7 g, keeping the other experimental parameters constant (i.e. pH: 2, contact time: 1 h and agitation speed: 150 rpm). The results given in Fig. 6 show that the percentage removal of Cr(VI) increased rapidly with increase in the quantity of the *Teff* straw. However, the maximum removal efficiency was exhibited for the adsorbent dose of 0.6 g which was found to be 93.2% and thus this dose was taken as optimum. This may mainly be due to the fact that availability of exchangeable sites for the ions increases with increase in the adsorbent doses [5] and beyond 0.6 g, the adsorption sites get saturated with the available Cr(VI) ions. As a result, further addition of the adsorbent has not brought about significant increase in the removal efficiency.

3.2.5. Effect of the initial metal ion concentration

To evaluate the effect of initial concentration of Cr(VI) on its percentage removal by the *Teff* straw, different concentrations in the range 2.5–15 mg/l (with interval of 2.5 mg/l), were investigated keeping all other experimental parameters constant. The percentage adsorption of Cr(VI) decreased with increase in the initial concentration. But, the actual amount of Cr(VI) adsorbed per unit mass of the adsorbent was increased with increase in the initial Cr(VI) concentration. In the case of low Cr(VI) concentrations, the ratio of the initial number of moles of Cr(VI) ions to the available surface area of the adsorbent is large and consequently the fractional adsorption becomes independent of the initial concentration [35]. However, at higher concentrations, the available sites for adsorption become fewer, and hence the percentage removal

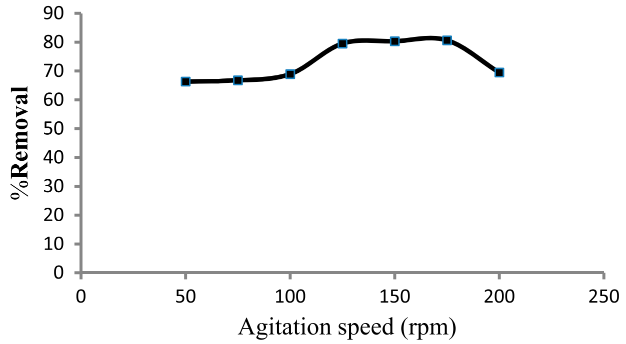

Fig. 4. Effect of agitation speed on percentage removal of Cr(VI).

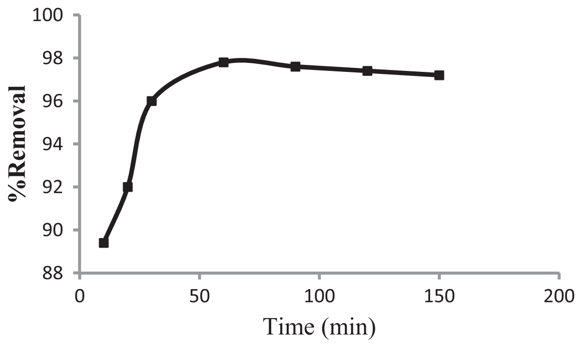

Fig. 5. Effect of contact time on percentage removal of Cr(VI) on the *Teff* straw.

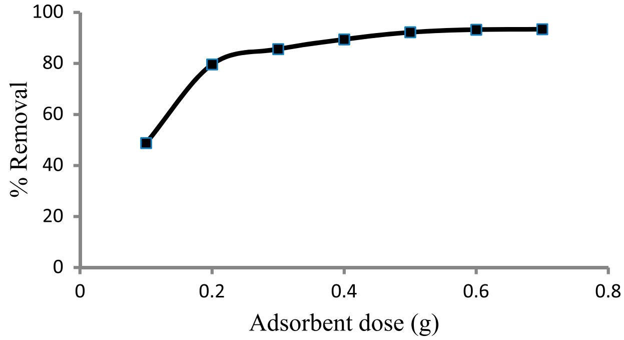

Fig. 6. Effect of the adsorbent dose on percentage removal of Cr(VI).

of the metal ions, which depends upon the initial concentration, decreased [36]. As shown in Fig. 7, the maximum percentage removal, 79.9%, was obtained for initial concentration of 5 mg/l. These results confirm that with increase in Cr(VI) concentration from 2.5 to 15 mg/l the percentage removal decreases from 83 to 73.3%.

3.3. *Adsorption isotherms*

Sorption equilibria provide fundamental physicochemical information for evaluating the applicability of the adsorption process [37]. In order to investigate the relationship between the quantity of the adsorbate sorbed (q_e) and the aqueous concentration at equilibrium (C_e), sorption isotherm models, *viz.* Langmuir and Freundlich equations are most frequently employed for evaluating the precision of the experimental data. The equilibrium results obtained in the current study were also evaluated using the aforementioned two isotherm models, in a similar manner, as has also been described by several other studies [38–40].

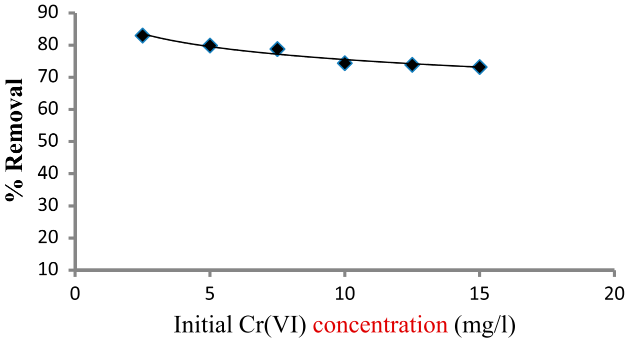

Fig. 7. Effect of initial adsorbate concentration on percentage removal of Cr(VI).

3.3.1. *Langmuir isotherm*

The Langmuir isotherm model makes several assumptions, such as monolayer coverage and constant adsorption energy of the process on uniform surfaces [41]. In the present study, the affinity between the adsorbent and Cr(VI) was quantified by fitting the obtained sorption results to the linear Langmuir equation, described below:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \left(\frac{1}{bQ_o}\right)\frac{1}{C_e} \tag{3}$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l), Q_o is the maximum sorption uptake (mg/g), and b is the Langmuir constant (l/mg), which is related to the affinity of the binding sites for the adsorbate. The values of b and Q_o were obtained from the slope and intercept of the plot, $1/q_e$ vs. $1/C_e$, respectively, as depicted in Fig. 8(a). The values obtained in this work for the maximum adsorption capacity, $Q_{o,}$ and the Langmuir constant, b, were found to be 3.51 mg/g and 0.33 l/mg, respectively.

The characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant, the separation factor (R_L). It indicates the shape of the isotherm which can be calculated by the formula given in Eq. (4) [42]:

$$R_L = \frac{1}{1 + bC_o} \tag{4}$$

where b is obtained from the Langmuir plot and C_o (mg/l) is the initial concentration of Cr(VI). In the present study, the value of R_L was found to be 0.38 indicating favorable uptake of Cr(VI) by the *Teff* straw [43].

3.3.2. *Freundlich isotherm*

The Freundlich isotherm model deals with physicochemical adsorption on heterogeneous surfaces [41]. It was derived to model multilayer adsorption and is formulated as follows:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{5}$$

where K_F is the Freundlich constant which indicates the adsorption capacity and represents the strength of the adsorptive bond while n is the heterogeneity factor

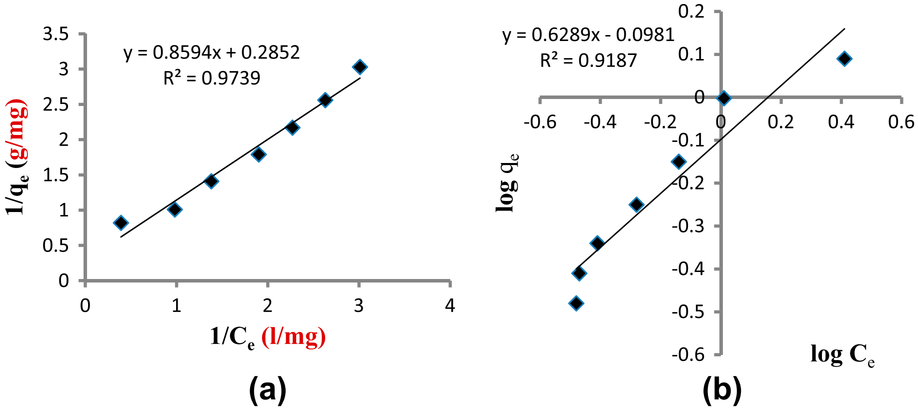

Fig. 8. Langmuir (a) and Freundlich (b) isotherms for Cr(VI) adsorption on the *Teff* straw.

representing the bond distribution and adsorption intensity [25]. The Freundlich equation can be described by the linearized form given in Eq. (6):

$$\log q_e = \log K_F + (1/n)\log C_e \tag{6}$$

The values of K_F and $1/n$ were obtained from the intercept and slope of the plot of log q_e vs. log C_e and were found to be 0.798 and 0.6289, respectively, as has also shown in Fig. 8(b). However, the higher correlation coefficient obtained from the Langmuir plot ($R^2 = 0.9739$) compared to the Freundlich plot ($R^2 = 0.9187$) confirmed monolayer coverage of the surface of the *Teff* straw by the Cr(VI) ions.

Thus, the Langmuir model was found to fit the Cr (VI) adsorption very well than the Freundlich model as has also been shown by the corresponding lower value of the linear regression coefficient (R^2), for the latter. The Langmuir parameters, Q_o and b, together with K_F and $1/n$ of the Freundlich parameters are given in Table 3.

3.4. Adsorption kinetics

Adsorption kinetics describes the solute adsorption rate and is important characteristic in evaluating the efficiency of adsorption [34]. Two vital evaluation elements for adsorption process are the mechanism and the reaction rate, where the rate determines the residence time required for completing the adsorption reaction and can be visualized from kinetic analysis [44]. In order to investigate the mechanism of sorption and potential rate-controlling steps such as mass transport and chemical reaction processes, kinetic models are commonly used to test experimental data [45]. To this end, pseudo-first and pseudo-second order models were applied in the current study.

3.4.1. Pseudo-first order kinetics

The pseudo-first order rate equation is generally expressed as follows [42]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{7}$$

where q_t (mg/g) is the concentration of Cr(VI) adsorbed at time t (min) and k_1 (min^{-1}) is the rate constant of the pseudo-first order equation. Integrating and rearranging (Eq. (7)) for the boundary conditions; $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$ gives the linear form expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{8}$$

The values of q_e and k_1 in (Eq. (8)) were obtained from the slope and intercept of the plot of log $(q_e - q_t)$ vs. t depicted in Fig. 9(a). The numerical values of q_e and k_1 determined in the current study were found to be 0.1 mg/g and 0.083 min^{-1}, respectively.

3.4.2. Pseudo-second order kinetics

When the rate of sorption follows the pseudo-second order mechanism, the chemisorption kinetic rate equation is expressed as [45]:

Table 3
The Langmuir and Freundlich constants for the adsorption of Cr(VI) on the *Teff* straw

Metal ion	Langmuir Q_o (mg/g)	b (l/mg)	R^2	R_L	Freundlich K_F (mg/g)/(mg/L)$^{1/n}$	$1/n$	R^2
Cr(VI)	3.51	0.33	0.9739	0.38	0.798	0.6289	0.9187

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

where k_2 (g/(mg min)) is the second-order rate constant for the pseudo-second order equation. Integrating (Eq. (9)) for the boundary condition; $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ and rearranging gives the following linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t = \frac{1}{h} + \frac{1}{q_e} t \tag{10}$$

The values of q_e and k_2 were obtained from the slope and intercept of the plot of t/q_t vs. t, described in Fig. 9(b), and were found to be 0.408 and 2.87, respectively. As shown in Table 4, the pseudo-second order model was found to fit the experimental data compared to the pseudo-first order model, which have been described by the respective values of R^2. Moreover, the theoretical value of q_e (0.408 mg/g) predicted from the pseudo-second order plot agrees well to the experimental one (0.407 mg/g). Therefore, in the present study, the adsorption of Cr(VI) on the *Teff* straw was found to follow pseudo-second order kinetic model which relies on the assumption that chemisorption or chemical adsorption is the rate-determining step [34].

3.5. Comparison of the performances of different adsorbents for Cr(VI) adsorption

Literature reports have revealed that different adsorbents have been utilized widely to remove different toxic heavy metals from environmental water samples. Some of the adsorbents used for removal of Cr (VI) are compared with the present work and the corresponding findings are shown in Table 5. It can be seen that pH 2 is optimum for most of the adsorbents considered. This is in line with the fact that Cr(VI) get reduced to Cr(III) to a large extent at pH close to 1 and the competition of OH ions with the Cr(VI) ions for the active sites at higher pH values could affect Cr (VI) adsorption [31]. The experimental data of the present investigation are favorably competent compared to the reported values. The adsorption capacity varies and depends on the characteristics of the individual adsorbent, the extent of surface modification, and the initial concentration of the adsorbate [46]. It is to be noted that *Teff* straw could be considered as one of the potential candidate to be used reliably for quantitative and efficient removal of toxic metals, such as Cr(VI), from contaminated complex matrices. Further advantages of using *Teff* straw are its low-cost, local availability, and environmentally friendliness as adsorbent to remove Cr(VI) and other structurally and characteristically related metals from environmental water samples.

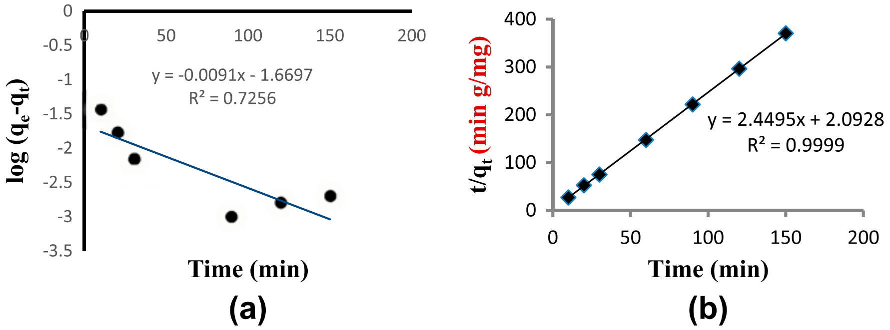

Fig. 9. Pseudo-first order (a) and pseudo-second order (b) kinetics of Cr(VI) adsorption on the *Teff* straw.

Table 4
Pseudo first and pseudo second order adsorption rate constants with the calculated and experimental q_e values for adsorption of Cr(VI) on the *Teff* straw

		Pseudo-first order			Pseudo-second order			
Metal ion	q_e (mg/g)*	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg min)	h (mg/g min)	R^2
Cr(VI)	0.407	0.1	0.083	0.8859	0.408	2.87	0.478	0.9999

*Experimentally obtained.

Table 5
Adsorption capacity of different adsorbents for Cr(VI) as reported in the literature

Adsorbent	Maximum adsorption capacity, Q_o (mg/g)	Optimum pH	Adsorbent dose (g)	Maximum concentration C_o (mg/l)	References
Wheat bran	0.942	3	2	5	[14]
Almond shell	3.40	3.2	0.5	–	[15]
Rice straw	3.15	2.0	–	–	[17]
Sugar cane bagasse	13.4	2.0	1	250	[47]
Eucalyptus bark	45	2.0	1.25	250	[48]
Coconut tree sawdust	3.46	3.0	–	20	[49]
Modified Sawdust	18.86	6.0	–	50	[50]
Rice bran	12.34	2.0	1	–	[51]
Teff straw	3.51	2.0	0.6	5	This study

4. Conclusion

In the present study, *Teff* straw was successfully utilized as a low-cost, locally available, and environmentally friendly adsorbent for the adsorption and removal of Cr(VI) from synthetic wastewater samples. The results obtained revealed that *Teff* straw has exhibited rapid adsorption rate and good adsorption capacity for Cr(VI). It was also found that the adsorption process in the current study was dependent on pH, contact time, agitation speed, adsorbent dose, and initial metal ion concentration. The adsorption of Cr (VI) was found to fit the Langmuir isotherm suggesting monolayer coverage of the adsorbent surface. The kinetic study also revealed that the adsorption process in the present study obeyed pseudo-second order model indicating chemisorption as the rate limiting step. Hence, *Teff* straw, an abundant low-cost biomaterial, which had a high Cr(VI) uptake capacity (3.51 mg/g), could be used as a good alternative adsorbent for quantitative removal of Cr(VI) from wastewater particularly tannery effluents.

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References

[1] R. Flouty, G. Estephane, Bioaccumulation and biosorption of copper and lead by a unicellular algae *Chlamydomonas reinhardtii* in single and binary metal systems: A comparative study, J. Environ. Manage. 111 (2012) 106–114.

[2] M.H. Isa, N. Ibrahim, H. Aziz, M.N. Adlan, N.H.M. Sabiani, A.A.L. Zinatizadeh, S.R.M. Kutty, Removal of Cr(VI) from aqueous solution using treated oil palm fibre, J. Hazard. Mater. 152 (2008) 662–668.

[3] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of Cr(VI) in industrial wastewater using low-cost abundantly available adsorbents, Adv. Environ. Res. 6 (2002) 533–540.

[4] C.M. Zvinowanda, J.O. Okonkwo, P.N. Shabalala, N.M. Agyei, A novel adsorbent for heavy metal remediation in aqueous environments, Int. J. Environ. Sci. Technol. 6 (2009) 425–434.

[5] S.P. Dubey, K. Gopal, adsorption of Cr(VI) on low cost adsorbents derived from agricultural waste material: A comparative study, J. Hazard. Mater. 145 (2007) 465–470.

[6] A. Esmaeili, A. Mesdaghinia, R. Vazirinejad, Cr(III) removal and recovery from tannery wastewater by precipitation process, Am. J. Appl. Sci. 2 (2005) 1471–1473.

[7] S. Rengaraj, K.H. Yeon, S.H. Moon, Removal of chromium from water and wastewater by ion exchange resins, J. Hazard. Mater. 87 (2001) 273–287.

[8] S. Rengaraj, K.H. Yeon, S.Y. Kang, J.U. Lee, K.W. Kim, S.H. Moon, Studies on adsorptive removal of Co(II), Cr(III) and Ni(II) by IRN77 cation-exchange resin, J. Hazard. Mater. 92 (2002) 185–198.

[9] S. Rengaraj, C.K. Joo, Y. Kim, J. Yi, Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H, J. Hazard. Mater. 102 (2003) 257–275.

[10] C.A. Kozlowski, W. Walkowiak, Removal of Cr(VI) from aqueous solutions by polymer inclusion membranes, Water Res. 36 (2002) 4870–4876.

[11] D. Mohan, C.U.J. Pittman, Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, J. Hazard. Mater. 137 (2006) 762–811.

[12] N. Das, R. Vimala, P. Karthika, Biosorption of heavy metals: An overview, Indian J. Biotech. 7 (2008) 159–169.

[13] K. Chojnacka, A. Chojnacki, H. Górecka, Biosorption of Cr^{3+}, Cd^{2+} and Cu^{2+} ions by blue–green algae Spirulina sp.: Kinetics, equilibrium and the mechanism of the process, Chemosphere 59 (2005) 75–84.

[14] M. Nameni, M.R. Alavi Moghadam, M.A. Arami, Adsorption of hexavalent chromium from aqueous solutions by wheat bran, Int. J. Environ. Sci. Technol. 5 (2008) 161–168.

[15] E. Pehlivan, T. Altun, Biosorption of chromium (VI) ion from aqueous solutions using walnut, hazelnut and almond shell, J. Hazard. Mater. 155 (2008) 378–384.

[16] S.R. Singh, A.P. Singh, Treatment of water containing chromium (VI) using rice husk carbon as a new low cost adsorbent, Int. J. Environ. Res. 6 (2012) 917–924.

[17] H. Gao, Y. Liu, G. Zeng, W. Xu, T. Li, W. Xia, Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste—Rice straw, J. Hazard. Mater. 150 (2008) 446–452.

[18] A. Maleki, A.H. Mahvi, M.A. Zazouli, H. Izanloo, A.H. Barati, Aqueous cadmium removal by adsorption on barley hull and barley hull ash, Asian J. Chem. 23 (2011) 1373–1376.

[19] U.K. Garg, M.P. Kaur, V.K. Garg, D. Sud, Removal of hexavalent chromium from aqueous solution by agricultural waste biomass, J. Hazard. Mater. 140 (2007) 60–68.

[20] U.S. Orlando, A.U. Baes, W. Nishijima, M. Okada, Preparation of chelating agents from sugarcane bagasse by microwave radiation as an alternative ecologically benign procedure, Green Chem. 4 (2002) 555–557.

[21] M. Sahranavard, A. Ahmadpour, M.R. Doosti, Biosorption of hexavalent chromium ions from aqueous solutions using almond green hull as a low cost biosorbent, Eur. J. Sci. Res. 58 (2011) 392–400.

[22] G. Bultosa, Physicochemical characteristics of grain and flour in 13 Tef [Eragrostis tef (Zucc.) Trotter] grain varieties, J. Appl. Sci. Res. 3 (2007) 2042–2051.

[23] M.I.O. Mohammed, A.I. Mustafa, G.A.M. Osman, Evaluation of wheat breads supplemented with Tef (Eragrostis tef (ZUCC.) Trotter) grain flour, Aust. J. Crop Sci. 3 (2009) 207–212.

[24] K. Sathasivam, H.M. Haris, Banana trunk fibers as an efficient biosorbent for the removal of Cd(II), Cu(II), Fe(II) and Zn(II) from aqueous solutions, J. Chil. Chem. Soc. 55 (2010) 278–282.

[25] G. García-Rosales, A. Colín-Cruz, Biosorption of lead by maize (Zea mays) stalk sponge, J. Environ. Manage. 91 (2010) 2079–2086.

[26] G.S. Agarwal, H.K. Bhuptawat, S. Chaudhari, Biosorption of aqueous chromium(VI) by *Tamarindus indica* seeds, Bioresour. Technol. 97 (2006) 949–956.

[27] M.T. Sulak, H.C. Yatmaz, Removal of textile dyes from aqueous solutions with eco-friendly biosorbent, Desalin. Water Treat. 37 (2012) 169–177.

[28] B. Singha, T.K. Naiya, A.K. Bhattacharya, S.K. Das, Cr (VI) Ions removal from aqueous solutions using natural adsorbents—FTIR studies, J. Environ. Prot. 2 (2011) 729–735.

[29] A.B. Pérez-Marín, V.M. Zapata, J.F. Ortuño, M. Aguilar, J. Sáez, M. Lloréns, Removal of cadmium from aqueous solutions by adsorption onto orange waste, J. Hazard. Mater. 139 (2007) 122–131.

[30] S. Guo, W. Li, L. Zhang, J. Peng, H. Xia, S. Zhang, Kinetics and equilibrium adsorption study of lead(II) onto the low cost adsorbent—Eupatorium adenophorum spreng, Process Saf. Environ. Prot. 87 (2009) 343–351.

[31] T. Karthikeyan, S. Rajgopal, L.R. Miranda, Chromium (VI) adsorption from aqueous solution by Hevea Brasilinesis sawdust activated carbon, J. Hazard. Mater. 124 (2005) 192–199.

[32] E.A. Oliveira, S.F. Montanher, M.C. Rollemberg, Removal of textile dyes by sorption on low cost sorbents. A case study: Sorption of reactive dyes onto Luffa cylindrical, Desalin. Water Treat. 25 (2011) 54–64.

[33] R. Shawabkeh, Equilibrium study and kinetics of Cu^{2+} removal from water by zeolite prepared from oil shale ash, Process Saf. Environ. Prot. 87 (2009) 261–266.

[34] S.C. Ibrahim, M.A.K.M. Honafiah, M.Z.A. Yahya, Removal of cadmium from aqueous solutions by adsorption onto sugarcane bagasse, Am-Eurasian J. Agric. Environ. Sci. 1 (2006) 179–184.

[35] S. Gupta, B.V. Babu, Removal of toxic metal Cr(VI) from aqueous solutions using sawdust as adsorbent: Equilibrium, kinetics and regeneration studies, Chem. Eng. J. 150 (2009) 352–365.

[36] L.J. Yu, S.S. Shukla, K.L. Dorris, A. Shukla, J.L. Margrave, Adsorption of chromium from aqueous solutions by maple sawdust, J. Hazard. Mater. 100 (2003) 53–63.

[37] N. Yeddou, A. Bensmaili, Equilibrium and kinetic modelling of iron adsorption by eggshells in a batch system: Effect of temperature, Desalination 206 (2007) 127–134.

[38] B. Yasemin, T. Zeki, Removal of heavy metals from aqueous solution by sawdust adsorption, J. Environ. Sci. 19 (2007) 160–166.

[39] G. Müller, K. Janošková, T. Bakalár, J. Cakl, H. Jiránková, Removal of Zn(II) from aqueous solu-

tions using Lewatit S1468, Desalin. Water Treat. 37 (2012) 146–151.

[40] S. Larous, A.H. Meniai, M.B. Lehocine, Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust, Desalination 185 (2005) 483–490.

[41] F.N. Acar, E. Malkoc, The removal of chromium(VI) from aqueous solutions by *Fagus orientalis* L. Bioresour. Technol. 94 (2004) 13–15.

[42] P.K. Malik, Dye removal from wastewater using activated carbon developed from sawdust: Adsorption equilibrium and kinetics, J. Hazard. Mater. 113 (2004) 81–88.

[43] E. Malkoc, Y. Nuhoglu, M. Dundar, Adsorption of chromium(VI) on pomace—An olive oil industry waste: Batch and column studies, J. Hazard. Mater. 138 (2006) 142–151.

[44] Y.S. Ho, Citation review of lagergren kinetic rate equation on adsorption reactions, Scientometrics 59 (2004) 171–177.

[45] Y.S. Ho, G. McKay, A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents, Process Saf. Environ. Prot. 76 (1998) 332–340.

[46] A.K. Bhattacharya, T.K. Naiya, S.N. Mandal, S.K. Das, Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents, Chem. Eng. J. 137 (2008) 529–541.

[47] D.C. Sharma, C.E. Forster, A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents, Bioresour. Technol. 47 (1994) 257–264.

[48] V. Sarin, K.K. Pant, Removal of chromium from industrial waste by using eucalyptus bark, Bioresour. Technol. 97 (2006) 15–20.

[49] K. Selvi, S. Pattabhi, K. Kadirvelu, Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon, Bioresour. Technol. 80 (2001) 87–89.

[50] M.S. Siboni, M.R. Samarghandi, S. Azizian, W.G. Kim, S.M. Lee, The removal of hexavalent chromium from aqueous solutions using modified holly sawdust: Equilibrium and kinetics studies, Environ. Eng. Res. 16 (2011) 55–60.

[51] B. Singha, S.K. Das, Biosorption of Cr(VI) ions from aqueous solutions: Kinetics, equilibrium, thermodynamics and desorption studies, Colloids Surf. B 84 (2011) 221–232.